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A theoretical framework for absorption (dichroism) and the resonance-enhanced scattering of X-rays by magnetic materials

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Abstract

The scattering length common to the attenuation coefficient and cross-sections for the resonance-enhanced scattering of X-rays suffers from a dependence on a spectrum of virtual, intermediate states which contain next to no useful information about the environment of the atoms. It is the dependence of the scattering length on intermediate states that sets the X-ray techniques apart from neutron scattering and other techniques which directly probe properties of magnetic materials, and limits the usefulness of physical intuition in the interpretation of empirical X-ray data. As a step toward a legible interpretation, in a language of standard atomic variables, an investigation is reported of a modified scattering length constructed to possess a structure similar to the scattering length for magnetic neutron scattering, namely, it has the mathematical structure of a spherical tensor operator, to which all Racah's methods for electrons in an open valence shell can be applied. In the process of reaching this goal, the influence of the intermediate states on the scattering length is reduced by summing over a limited set of quantum numbers for the intermediate states. Topics covered in the investigation include the attenuation coefficient for X-rays passing through a foil of magnetic material, dichroism, and the cross-sections for resonance-enhanced elastic (Bragg) and inelastic scattering of X-rays by magnetic materials. The treatment of polarization in the primary beam admits states of partial polarization, described by a Stokes vector. Both *jj*-coupling and Russell-Saunders coupling schemes for the valence states are explored.

§1 Introduction

In the past decade, experimental techniques that employ beams of X-rays have proved their worth for the study of the magnetic properties of materials (for a review see [1]). For the most part using beams of X-rays produced by particle accelerators, a raft of experiments have been successfully completed on a wide range of magnetic materials.

Two of the techniques, absorption and scattering, are truly complementary since the interpretation of the empirical data rests on a common scattering length. In terms of the scattering length, f, the attenuation coefficient is proportional to the imaginary part of f evaluated for the forward scattering geometry and averaged over all states of the target material. On the other hand, scattering experiments are interpreted in terms of a scattering cross-section which is a quadratic function of the scattering length. The cross-section for Bragg diffraction, a strictly elastic process, is proportional to $|\langle f \rangle|^2$ where $\langle f \rangle$ is the time (thermal) average of f. Inelastic and total scattering experiments are properly interpreted in terms of a cross-section related to $\langle |f^2| \rangle$.

For processes involving X-ray absorption and scattering the content of the measured signal attributable to the magnetic properties of the sample, altogether, is pale and insignificant in its intensity, compared to the intensity of contributions to the signal arising from the electric charge properties of the material. At least for the moment, success in studying magnetic properties with X-ray beam techniques hinges on adopting a scheme to enhance the magnetic signal with respect to the charge signal. In absorption experiments one exploits the sensitivity of the attenuation coefficient to the condition of the polarization in the primary beam, a so-called dichroic effect. Use of circular polarization is very useful. A scheme for enhancing scattering signals is to tune the energy of the primary beam to the energy of a resonance in the magnetic atom of interest. Resonance-enhanced scattering, as it is sometimes called, has proved useful with materials which contain magnetic atoms from the lanthanide and actinide series in the Periodic Table.

Turning to the interpretation, at an atomic level of detail, of dichroic signals and resonance-enhanced scattering, both are related to the contribution to f generated by the current operator treated in the second order of perturbation theory. It is the energy denominator in this contribution to f that generates the first-order contribution to the attenuation coefficient. Tuning the energy of the primary beam to a resonance means finding an energy at which the real part of the denominator vanishes, with a concomitant enhancement of the corresponding cross-section (elastic and inelastic processes can be resonance-enhanced). The resonance process entails the absorption of a photon, and ejection of an electron from a core state of the equilibrium configuration of the atom to an orbital which is unoccupied. These virtual, intermediate states, characterized by a hole in a core state, are not states of the equilibrium configuration of the electrons. While necessary in the resonance process, of course, the intermediate states are an unwelcome distraction in the interpretation of empirical data. A full account of the intermediate states which arise in elements that possess open valence shells, and display magnetic properties in solids, can only be achieved with the resource of a computer program to calculate the full atomic structure. There is one exception, namely, an atom for which the open valence shell of the equilibrium configuration contains one hole; in all other cases a tried and tested computer program is required to enumerate the plethora of intermediate states and provide their energies and wave functions (and matrix elements); see for example listings given in [2,3].

While the intermediate states cannot be entirely removed in a quantitative interpretation of empirical data, perhaps one can achieve a tolerable interpretation with less than the full information on the intermediate states. An aim of the paper is to report a scheme in which the intermediate states are largely eliminated from the calculation of the scattering length. It is argued that information, on the magnetic properties of the material, carried in the valence orbitals is not unduly distorted by the process of elimination. With the idealized scattering length, calculations of the attenuation coefficient and cross-sections, for elastic and inelastic resonance-enhanced scattering, are made with the standard tools of atomic spectroscopy. Many of the quantities involved, e.g. Racah's unit tensor operators for equivalent electrons, are

widely available in analytic or tabular form. Our calculations make quite explicit the complementary nature of absorption and resonance-enhanced scattering. For a special case, in which the valence orbitals are represented by one atomic wave function, we recover results given in [1].

The following section contains the definition of the scattering length which describes the attenuation and resonance-enhanced scattering of X-rays, and the simplification brought to it by the neglect of the contribution explicit in the spin of the electrons and a treatment at a first level of approximation of the momentum of the electrons. The derivation of our formula, which we later call an *idealized* scattering length, in the form of a spherical tensor, is described in an appendix. Section 3 is given over to a summary of its properties with a view to applying it to the calculation of the attenuation coefficient and cross-sections, which are taken up in three subsequent sections. We conclude with a brief summary of our findings.

§2. **Resonant component of the scattering length**

Throughout the paper we consider the component of the scattering length for a beam of X-rays that arises from treating the current operator, $\mathbf{J}(\mathbf{q})$, in the second order of perturbation theory. (Other terms in the scattering length arise from contributions to the X-ray-matter interaction which are quadratic in the vector potential of the photons and, hence, treated in the first order of perturbation theory.) The resonant component of the scattering length, f, is characterized by an energy denominator whose real part is zero for a suitable energy, E, of the primary beam of X-rays. At the condition of resonance, the denominator has a magnitude set by the (decay) width in energy, γ, of the intermediate states in the resonance process, labelled by η. Unlike the initial and final states of the sample, described by quantum numbers μ and μ', respectively, the intermediate states are not from the equilibrium configuration of the sample.

Let the wave vector and polarization vector of the primary photon beam be $\mathbf{q}$ and $\boldsymbol{\varepsilon}$, respectively, with $q = (2\pi/\lambda)$. The corresponding quantities for the secondary

beam are distinguished by a prime. The resonant contribution to the scattering length is [1],

$$f = -(r_e / m)\sum_{\eta} \frac{\langle \mu' | \varepsilon' . \mathbf{J}(-\mathbf{q}') | \eta \rangle \langle \eta | \varepsilon . \mathbf{J}(\mathbf{q}) | \mu \rangle}{(E_\mu + E - E_\eta + i\gamma_\eta / 2)},$$

where r_e is the classical radius of an electron ($r_e = 0.282 \times 10^{-12}$ cm) and m is the mass of an electron. At the condition of resonance for the intermediate state η_0 the difference in energy between the intermediate and initial state of the target, $\left(E_{\eta_0} - E_\mu\right)$, is matched by E. For this condition the contribution to f from all other intermediate states is relatively small. The dimension of f is length.

The current operator contains a sum over all electrons in the target sample. We consider resonant processes that are specific to a particular atom in the sample. Hence, it is appropriate to express $\mathbf{J}(\mathbf{q})$ as the combined sum over all these atoms, at positions in the sample denoted by $\{\mathbf{R}_0\}$, and the sum over all electrons in the atom located at $\mathbf{R}_0$. Given that there is no correlation between the resonant electronic processes at different atoms the scattering length is,

$$f = -(r_e / m)\sum_{\mathbf{R}_0} \exp(i\,\mathbf{k}.\mathbf{R}_0)\sum_{\eta} \left\{ \frac{\langle \mu' | \varepsilon' . \mathbf{J}(-\mathbf{q}') | \eta \rangle \langle \eta | \varepsilon . \mathbf{J}(\mathbf{q}) | \mu \rangle}{(E_\mu + E - E_\eta + i\gamma_\eta / 2)} \right\}_{\mathbf{R}_0}, \qquad (2.1)$$

with $\mathbf{k} = \mathbf{q} - \mathbf{q}'$. The spatial phase factor in (2.1) is determined by the corresponding quantity in the current operator, given explicitly later in this section, and the actual form in which the product of current operators arises in the scattering length. In the expression (2.1), which is the basis of all our subsequent work on absorption and scattering, the matrix elements are calculated for the atom at site $\mathbf{R}_0$; the condition of an atom, in general, will depend on its position in the sample, e.g. the axes of quantization will change, on account of the magnetic order, on moving from one atom to another.

The attenuation coefficient and cross-section for elastic (Bragg) scattering are calculated from the scattering length evaluated for elastic events. In this instance, one takes $\mu = \mu'$ and averages the scattering length over the degeneracy of equilibrium states weighting them by the degeneracy factor and thermal population factor. In the case of an isolated atom the quantum numbers $\{\mu\}$ are J and M, where J is the total angular momentum and M is the magnetic quantum number. The sum to be performed to obtain the scattering length for absorption and Bragg diffraction is a sum over the $(2J+1)$ values of M, and the weight of each M-state is $1/(2J+1)$. In the event the degeneracy is lifted by a magnetic field (either an applied field or an effective field generated by neighbouring atoms) each M-state will be weighted by a thermal population factor = $\exp(Mu)/\Xi$ where Ξ is the partition function. For inelastic scattering events, the cross-section is obtained from the absolute square of f multiplied by a delta function which expresses the conservation of energy in the event. The total cross-section is proportional to this quantity averaged over all initial states and summed over all final states.

The current operator in (2.1) is built from the operators of linear momentum, **p**, which is conjugate to the position vector **R**, and spin, **s**. If the electrons in the atom, at the site defined by $\mathbf{R}_0$, are labelled by the index j,

$$\mathbf{J(q)} = \sum_j (\mathbf{p}_j + i\hbar \mathbf{s}_j \times \mathbf{q}) \exp(i\mathbf{q}.\mathbf{R}_j).$$

In subsequent work we set aside the spin term in **J(q)**, on the grounds that its contribution to the required matrix element of **J(q)** is small relative to the contribution made by the momentum operator. Furthermore, we adopt the dipole approximation for the momentum contribution, for the moment at least. In this case, a matrix element of **J(q)** in (2.1) is independent of **q**, and,

$$\langle \eta | \varepsilon.\mathbf{J(q)} | \mu \rangle = (im/\hbar)(E_\eta - E_\mu) \sum_j \langle \eta | \varepsilon.\mathbf{R}_j | \mu \rangle. \qquad (2.2)$$

The magnetic content of the matrix element in (2.2) is carried by the initial, valence state of the atom, labelled by μ, and a similar comment is valid for the final state of the atom, μ', in the second matrix element appearing in the resonant contribution to the scattering length. It follows from (2.2) that, the magnetic features of the atoms in question are probed by electric dipole (E1) transitions.

§3. Idealized scattering length

The wave function of the core state in the resonant contribution to the scattering length, *f*, has a relatively small radius and the binding energy of the state is large. In consequence, the properties of the core state do not carry very much information about the environment of the atom. This situation is in strong contrast to the orbitals of the weakly bound electrons in the partially filled valence shell. If the objective of the experiment, be it a measurement of an attenuation coefficient or a scattering cross-section, is to learn about the environment of the atom the properties of the valence orbitals, and not the core states, are the appropriate focus of attention in the interpretation of empirical data. From this standpoint, the variables for the core state are irrelevant variables.

The spectrum of the intermediate states, belonging to an excited configuration in which there is a hole in a core state and the ejected electron occupies a valence state, contains very many components. The presence of the intermediate states in the scattering length make it inscrutable in terms of quantities and concepts central to the development of our understanding of magnetism. Of course, not all the components contribute to the sum over intermediate states in *f* because of the operation of selection rules for matrix elements of the dipole operator, say. Even so, the spectrum of components that contribute is complicated, for all but the simplest case of interest in which the valence shell of the equilibrium configuration contains a single hole, e.g. Yb^{3+}.

The two aspects of the intermediate states described in the preceding paragraphs make it clear that the possibility of removing the intermediate states from the

interpretation of the data is an attractive prospect. Should the latter step be achieved in a sufficiently delicate manner the remaining information in the interpretation will not be adversely affected too much. We set out to reduce the influence of the intermediate states in the formula for the scattering length and, in so doing, loose a minimal amount of useful information about the environment of the atom which is carried by the valence orbitals.

The environment influences the geometrical aspect of a wave function, e.g. the distribution of the magnetic quantum numbers, among other things. Hence, in eliminating information about the intermediate states in the scattering length we do not want to unduly distort the dependence of the product of matrix elements and the energy denominator on the magnetic quantum numbers associated with the initial and final states, of the equilibrium configuration of the atom. To this end, we can require that the magnetic quantum numbers arise in the product of matrix elements and the associated energy denominator, after largely eliminating the intermediate states, in the manner we find for a simple, direct probe of their character, with no intermediate states. Such a probe has an interaction operator, which contains a sum of atomic variables, that has the property of a spherical tensor operator. For example, in the scattering of neutrons by a magnetic atom the appropriate operator is the total angular momentum, in a useful approximation. Our concept, therefore, is to find the tensor operator which corresponds to the criteria we have set. Let the spherical tensor operator in question be T_Q^K, where K is the rank of the tensor and $-K \le Q \le K$. The Wigner-Eckart theorem applied this operator is,

$$\left\langle JM\left|T_Q^K\right|J'M'\right\rangle = (-1)^{J-M}\begin{pmatrix} J & K & J' \\ -M & Q & M' \end{pmatrix}\left(J\|T(K)\|J'\right). \tag{3.1}$$

The 3j-symbol contains the geometrical character of the matrix element in so far as it contains the magnetic quantum numbers M, and M'. The remaining quantity, a reduced matrix element, does not depend on M, and M'. Our goal, then, is to leave the scattering length, after eliminating some information on the intermediate states, in a form where matrix elements of the scattering length satisfy (3.1).

Let us now set out a plausibility argument for the technical side of what is involved in deriving an idealized scattering length, and this amounts to making a judicious choice of labels in the set η over which to sum and executing the sum without approximation. The latter exercise is relegated to an appendix, for even though it uses identities familiar to students of nuclear shell theory and atomic spectroscopy the details, at first sight, might fog the view of our goal. Also in the appendix is a summary of what we need from Racah's work on handling equivalent particles in terms of unit tensor operators. To indicate that our goal is reachable, at a cost to be quantified, we recall the standard formula for the product of two spherical harmonics in which the product is expressed as a linear combination of single spherical harmonics. A dipole operator is proportional to a spherical harmonic of rank one, and the scattering length (2.1) contains a product of their matrix elements. Hence, the product formula for spherical harmonics has the structure we seek for the scattering length. Further encouragement is found in the formula for the reduced matrix element of a tensor operator formed from the product of two tensors that act on the same part of a system (in our case, the spatial part of wave functions). Let the two tensor operators be of rank K_1 and K_2, and denote the operators by T_1 and T_2, and their tensor product by T. Since the addition of three angular momentum variables, K, K_1 and K_2, is involved in creating T from T_1 and T_2 the formula for the reduced matrix element of T (e.g. equation 15.23 in reference [4], and problem 1.6 in [5]) contains a 6j-symbol. The formula in question has the form,

$$\left(J\|T(K)\|J'\right) \propto \sum_{\bar{J}} \left(J\|T_1(K_1)\|\bar{J}\right)\left(\bar{J}\|T_2(K_2)\|J'\right)\begin{Bmatrix} K_1 & K_2 & K \\ J' & J & \bar{J} \end{Bmatrix}. \tag{3.2}$$

From this formula we can infer that to achieve the desired form for the scattering length, namely, a spherical tensor, the sum over the intermediate states, labelled η in (2.1), runs over the angular momentum label, $\bar{J}$, of the intermediate states. By implication, the sum in (2.1) is to include, with $\bar{J}$, the magnetic quantum number, $\bar{M}$, which removes from the scattering length the geometrical information on the intermediate states. (Formula (3.2) is introduced simply for the purpose in our

presentation of making plausible the outcome of the calculation described in the appendix, which makes no use of (3.2).) The price to be paid in carrying through the steps described is the neglect in the energy denominator of the dependence of the transition energy on the relevant part of the quantum label η. The energy is now replaced by a mean value for the distribution of energy levels covered by the quantum numbers $\bar{J}$ and $\overline{M}$ in η.

The error in the interpretation of empirical data, caused by discarding in the scattering length the dependence of the energy denominator on η, will be small if the spread in energy of the states labelled by $\bar{J}, \overline{M}$ is sufficiently small. Here, two other energy scales are relevant, namely, the total decay width, Γ, and the resolution in energy available in the experiment. If the spread in energy of the $\bar{J}$-states is similar or, better, smaller than these energies the loss of useful information in the interpretation will be modest, and possibly tolerable. A related consideration refers to the observed relative weight of contributions that can be labelled by the total angular momentum of the core state which participates in absorption. A good example of the dominance by one partner over the other is observed in uranium; the dichroic signal at the $3d_{3/2}$ edge is very strong relative to the signal at the $3d_{5/2}$ edge.

By way of illustrating the energies involved in the discussion we briefly consider data for absorption at some d-core states: 3d-4f ($M_{4,5}$), 4d-4f ($N_{4,5}$) and 4d-5f. For the lanthanides absorption at the $N_{4,5}$ edges occurs in the soft region of the X-ray spectrum (100 - 200 eV) and the spread in energy of the intermediate states is around 20 eV [2,6]. The $M_{4,5}$ edges of the lanthanides are in the region 830 - 1520 eV of the X-ray spectrum. The major absorption peaks are assigned to the core states $3d_{5/2}$ and $3d_{3/2}$ whose separation in energy increases from 16 eV for La to 45 eV for Tm, and the associated decay widths vary from 0.2 eV to 0.6 eV [3]. We also mention the 4d-5f transition in ^{92}U, reference [7]. In this case, the separation in energy of the core states is estimated to be about 40 eV, and $\Gamma \cong$ 2 eV. Of course, our idealized scattering length incorporates a sum over the core states, so it lacks detail on a scale attributable to the structure in the intermediate-state spectrum created by the individual identities of the $d_{5/2}$ and $d_{3/2}$ core states. Lastly, we note a recent and careful investigation of

circular dichroism in uranium monosulphide places a ±30% uncertainty in the scaling of the measured dichroic signal [13].

The formula proposed for the scattering length is derived in appendix A; henceforth, it is referred to as an *idealized* scattering length in view of the reduction in the information it contains on the intermediate states. The idealized f has a structure which can be inferred from the two formulae cited in the foregoing discussion, scilicet, it is a sum of tensor operators of rank K. Referring to (3.2), for the matrix elements in the scattering length $K_1 = K_2 = 1$, and the rank of the tensors is correct in the dipole limit to the current operator given by (2.2). The coupling of K, K_1 and K_2 obeys a triangular condition, from which it follow that $K = 0$, 1 and 2.

Let us add a few words about the choice of quantum numbers of the intermediate states that are summed over in creating the idealized scattering length. The choice of $\bar{J}$ and $\overline{M}$ appears to be the minimal set required to bring the product of matrix elements to a structure of a spherical tensor (actually a sum of three spherical tensors labelled by their rank K). These quantum numbers are *not* a complete set, of course. A sum on all quantum numbers required to define the intermediate states can be accomplished by using the property of closure. In this case one also reaches a function for the product of matrix elements which is a sum of spherical tensors, created by spherical harmonics. However, the function contains no information at all about the core state, and the sum of spherical harmonics does not contain a spherical harmonic of rank one. As we shall presently see, the tensor of rank one in the idealized scattering length carries information about the magnetic moment of the absorbing atom. We conclude that, a sum over all quantum numbers, accomplished by the property of closure, leads to a serious loss of useful information about the magnetic atom.

Because the idealized f is proportional to spherical tensors all the algebra for such tensors at our disposal is readily applied. In particular, the matrix elements of the idealized f for a valence shell with two or more holes can be written down, in terms of Racah unit tensor operators, directly from a knowledge of the matrix element

for one hole in the valence shell. We provide the unit tensors for both *jj*- and Russell-Saunders (*SL*-coupling) coupling schemes for spin (*S*) and orbital (*L*) angular momentum of the ground states obtained by applying Hund's rules. Here, we gather the essential material for the idealized scattering length with a view to using it to describe absorption and resonance-enhanced scattering by magnetic materials.

Let Δ be a mean value for the separation in energy between the initial state, μ, and the intermediate states, η. The corresponding quantity for the intermediate states and the final state, μ', is Δ' ($= E_\eta - E_{\mu'}$). The states labelled μ and μ' belong to an equilibrium configuration of the atom. The primary radiation has an energy $E = (2\pi\hbar c/\lambda)$, wave vector $\mathbf{q}$ and polarization vector ε. (Cartesian components of ε are purely real.) The corresponding quantities for the secondary beam carry a prime. The scattering vector $\mathbf{k} = \mathbf{q} - \mathbf{q}'$, and the atoms are at positions defined by vectors $\{\mathbf{R}_o\}$.

For an atomic orbital the labels in the initial and final atomic state are $\mu = \theta JM$, and $\mu' = \theta' J' M'$. The idealized scattering length appropriate for the description of the scattering of X-rays with an energy E close to Δ is,

$$f(\mu,\mu') = -\left(\frac{2\pi e}{\lambda}\right)^2 \left(\frac{\Delta'}{\Delta}\right)\{E - \Delta + i\Gamma/2\}^{-1} \sum_{\mathbf{R}_0} \exp(i\mathbf{k}\cdot\mathbf{R}_o)\, Z(\mu;\mu':\mathbf{R}_o). \tag{3.3}$$

Here, Z is created from the matrix element Υ defined in (A.4);

$$Z(\mu;\mu':\mathbf{R}_o) = \sum_{qq'} (\varepsilon'_q \varepsilon_{q'})^* \, \Upsilon_{qq'}(\mu;\mu':\mathbf{R}_o)\ . \tag{3.4}$$

The idealized scattering length (3.3) is used later to discuss resonance-enhanced scattering. The corresponding expression for the attenuation coefficient, γ, is also conveniently expressed in terms of Z. In this instance, though, Z is evaluated for the condition of elastic scattering and a forward scattering geometry ($\mathbf{q} = \mathbf{q}'$). Also, the mean value of Z for this condition occurs in γ averaged with respect to states of

polarization in the primary beam. We denote the mean value of Z averaged with respect to the polarization by $\langle Z\rangle_0$. The appropriate formula for the attenuation coefficient is,

$$\gamma = 2\pi\lambda n_0\left(\frac{e\Delta}{\hbar c}\right)^2 \delta(E-\Delta)\langle Z\rangle_0, \tag{3.5}$$

where n_0 is the density of particles in the target foil. In arriving at the formula (3.5) we have exercised the limit $\Gamma \to 0$ and this creates the delta function, which is zero unless $E = \Delta$. The action of the delta function sets $\lambda = (12.40/\Delta)$Å with Δ expressed in units of keV.

The function $Z(\mu;\mu')$ has the dimension (length)^2. It is convenient to introduce quantities C, D and E which contain, respectively, the reduced matrix element of the tensors $T(0)$, $T(1)$ and $T(2)$ multiplied by the other factors in (A.4), from which $Z(\mu;\mu')$ is constructed according to its definition (3.4). The value of D does not depend explicitly on the number of particles in the open valence shell. In fact, all tensors of an odd rank — D is built from $T(1)$ — have the remarkable property of being independent of the number of particles and diagonal with respect to the seniority quantum number. The value of D is determined solely by the quantum numbers which define the initial and final states in the matrix element Z.

Specializing to the case $\bar{l} = l - 1$, and using results presented in appendix A, we find:

Russell-Saunders coupling; l^n configuration, $n_h = 2(2l+1) - n$, and $\theta = \nu SL$ where ν is the seniority quantum number.

$$C = C(\theta J;\theta' J') = \tfrac{1}{3} n_h\, \delta_{J,J'}\, \delta_{\theta,\theta'}\, \frac{l}{(2l+1)} \langle l|R|l-1\rangle^2 ,$$

$$D = D(\theta J;\theta' J') = \delta_{\theta,\theta'} \frac{(L\|L\|L)}{2(2l+1)}\left[(2J+1)(2J'+1)\right]^{1/2} (-1)^{1+S+J+L} \begin{Bmatrix} J' & L & S \\ L & J & 1 \end{Bmatrix} \langle l|R|l-1\rangle^2 ,$$

and,

(3.6)

$$E = E(\theta J;\theta' J') = \tfrac{1}{6}\left\{\frac{l(l+1)(2l+3)}{(4l^2-1)}\right\}^{1/2} (\theta J\|T(2)\|\theta' J')\langle l|R|l-1\rangle^2 .$$

An extensive tabulation of 3j- and 6j-symbols is found in reference [15]. Table 1 contains values of the unit tensor operator $V(2)$ needed to calculate the reduced matrix element of $T(2)$.

***jj*-coupling;** j^n configuration, $n_h = (2j+1) - n$. Some applications of *jj*-coupling to describe magnetic properties of rare earth atoms are found in reference [10], where the main thrust is the theory of elastic and inelastic scattering of neutrons, and reference [7].

$$C = C(\nu J;\nu' J') = \tfrac{1}{3} n_h \delta_{J,J'} \delta_{\nu,\nu'} \frac{l}{(2l+1)} \langle l|R|l-1\rangle^2 ,$$

and for $2 \le n_h \le (2j-1)$,

$$D = D(\nu J;\nu' J') = \delta_{J,J'}\delta_{\nu,\nu'} \frac{(J\|J\|J)}{2(2l+1)} (2-g)\langle l|R|l-1\rangle^2, \qquad (3.7)$$

where g is the Landé factor. For $n_h = 1$ and $n_h = 2j$ the quantity D is obtained from (6.4) using for the reduced matrix element the value given in (A.5), which is appropriate for one particle. Note in (3.7) that both C and D are diagonal with respect to J and ν. The quantity E is the same as for the SL - coupling with the reduced matrix element of $T(2)$ replaced by $(\nu J\|T(2)\|\nu' J')$; see table 1. For the particular case $J = J'$, which applies, at a first level of approximation, in the interpretation of

the attenuation coefficient and elastic scattering cross-section, the quantity D has the same structure in the two coupling schemes we employ.

At this juncture we can usefully summarize the properties of the scattering length when the number of holes in the valence shell is assigned its boundary values. For $n_h = 0$ the quantities C, D and E are zero, and so is the resonance-enhanced scattering length, i.e. if the valence shell in question is fully occupied by electrons the envisaged resonance process, involving a transfer of a hole from an equilibrium configuration of the valence shell to a core state, is forbidden. The conjugate state $n_h = (2j+1)$, or $2(2l+1)$, is characterized by the values $D = E = 0$, while C attains its maximum value. Hence, as it is physically obvious, when there are no electrons in the valence shell there is no information in the experiments in question, other than the total number of holes in the valence shell.

In carrying out the sum over the components of the polarization vectors in the definition of Z, equation (3.4), we profit from a compact notation based on a spherical tensor,

$$X_Q^{(K)} = \sum_{qq'} \varepsilon'_q \varepsilon_{q'} (1q1q'|KQ) \ . \tag{3.8}$$

In (3.8) we use a standard definition of a tensor formed using a Clebsch-Gordan coefficient. A summary of the properties of $X_Q^{(K)}$ used in this paper is provided in table 2. Here we note that, $X_Q^{(1)}$ can be expressed as a linear combination of the Cartesian components of the vector product of the polarization vectors. No such simple interpretation exists for $X_Q^{(2)}$.

In the setting of (3.4) the components of $(\varepsilon' \times \varepsilon)$ and $X_Q^{(K)}$ are with respect to the axes of the magnetic atom at the site defined by the vector $\mathbf{R}_0$. Hence, as indicated in (3.4), the matrix element Z depends on $\mathbf{R}_0$, although we may not always display it. In general, the axes will change on moving from one atom to another, in a

manner that depends on the order adopted by the magnetic atoms, e.g. antiferromagnetic, spiral, etc. The Cartesian components of a vector in the axes of quantization for the magnetic atom are labelled (a, b, c).

For some purposes, it is perspicacious to have a symmetric and compact notation for the matrix element Z. To this end we introduce another tensor $I^{(K)}$ with $K = 1$ and 2 whose reduced matrix element is one. The scalar product of I and X is defined, for all K, by,

$$\mathbf{I} \cdot \mathbf{X} = \sum_{q} (-1)^q I_q X_{-q} , \tag{3.9}$$

where $-K \le q \le K$. For $K = 1$ the definition (3.9) is identical to the conventional scalar product of two vectors. With this notation we arrive, directly from (3.4), (3.8), and (A.4), at,

$$Z(\theta JM;\theta' J'M') = \left\langle JM \middle| \left\{ (\boldsymbol{\varepsilon}' \cdot \boldsymbol{\varepsilon}) C + D\sqrt{2}\, \mathbf{I}^{(1)} \cdot \mathbf{X}^{(1)} - E\sqrt{6}\, \mathbf{I}^{(2)} \cdot \mathbf{X}^{(2)} \right\} \middle| J'M' \right\rangle . \tag{3.10}$$

This formula for Z is one of our key results. The three parts of Z have direct physical interpretations, as it will emerge in subsequent applications to various problems. Anticipating these applications, to some extent, we remark now that the first part of Z on the right hand side of (3.10) is an isotropic term with no magnetic content. The second and third parts have magnetic content, related, respectively, to the magnetic and quadrupole moment of the atom. In the particular case $J = J'$ it is useful to use operator equivalents for I, i.e. represent I with X as defined in table 2 and use for **t** and **u** the total angular momentum operator. We have more to say on this topic in subsequent sections.

While the representation of our result used in (3.10) has much to recommend it, particularly in applications to events pertaining to one J-manifold, there are occasions

when a more explicit representation of $Z(\theta JM;\theta'J'M')$ is useful. It can be written as the sum of the following terms, labelled by the value of m_o.

$m_o = 0$:

$$(\varepsilon'\cdot\varepsilon)\,C + (-1)^{J-M}\left[\begin{pmatrix} J & 1 & J' \\ -M & 0 & M \end{pmatrix} iD(\varepsilon' x \varepsilon)_o + \begin{pmatrix} J & 2 & J' \\ -M & 0 & M \end{pmatrix} E(\varepsilon'\cdot\varepsilon - 3\varepsilon'_o\varepsilon_o)\right].$$

$|m_0| = 1$:

$$(-1)^{J-M}\sqrt{2}\left\{-\begin{pmatrix} J & 1 & J' \\ -M & m_0 & M-m_0 \end{pmatrix} DX^{(1)}_{-m_0} + \begin{pmatrix} J & 2 & J' \\ -M & m_0 & M-m_0 \end{pmatrix} E\sqrt{3}\,X^{(2)}_{-m_0}\right\}. \quad (3.11)$$

$|m_0| = 2$:

$$(-1)^{J+1-M}\begin{pmatrix} J & 2 & J' \\ -M & m_0 & M-m_0 \end{pmatrix} E\sqrt{6}\,X^{(2)}_{-m_0}$$

The term with $m_0 = 0$ in (3.11), which is consistent with a cylindrical symmetry of the valence shell wave function, is exactly the quantity used in references [1,9]. In the latter works, the quantities C, D, and E, for one hole in the valence shell, are given as a sum over the total angular momentum quantum number, which labels the intermediate states, of the product of two reduced matrix elements of the dipole operator. Here, the sum over the product of nj-symbols is carried out, using the method described in the appendix, and gives the values for C, D, and E quoted in (3.6) and (3.7).

§4 Attenuation coefficient

The attenuation coefficient is calculated from formula (3.5). At a first level of approximation, the thermal average value of Z which enters (3.5) is derived from (3.11) evaluated for $\theta = \theta'$ and $J = J'$. The wave functions are linear combinations

of several states within the J-manifold, with coefficients determined by the physical and chemical properties of the absorbing atom.

In general, the ground state configuration is not a state with a unique θ and J. Spin-orbit magnetic interactions and electron-electron Coulomb interactions mix states of different θ and J into the state determined by Hund's rules. The formulae given in the previous section, for the quantities C, D, and E, permit a treatment of a general case. As might be anticipated, the physical interpretation of results for the idealized scattering length in the general case is not as simple and elegant as for a pure θ and J state. To see this look at $D(\theta J;\theta' J')$ for Russell-Saunders coupling. This quantity is diagonal with respect to θ and not diagonal in J and J', and for $J' = J \pm 1$ one does not have a nice result like D proportional to $(2 - g)$. Having sounded this note of caution about the likely structure of a realistic ground state, we continue in this, and the next section, by way of an illustration, to consider a ground state of the absorbing atom built from a J-manifold and a unique value of θ.

Within a J-manifold we can adopt the familiar practice of using operator equivalents, for $\mathbf{I}^{(1)}$ and $\mathbf{I}^{(2)}$, based on the operators of total angular momentum [8]. It seems natural to choose $\mathbf{J}$ to represent the operator $\mathbf{I}^{(1)}$, and, since this operator has been defined to have a reduced matrix element equal to one we need, $\mathbf{I}^{(1)} = \mathbf{J}/(J||J||J)$, where $(J||J||J) = \{J(J+1)(2J+1)\}^{1/2}$. It is convenient to represent $\mathbf{I}^{(2)}$ by an operator, denoted by $\mathbf{Q}$, constructed in accord with the tensor of rank 2 whose elements are listed in table 2, i.e. $\mathbf{Q}$ has the same structure as the combination of polarization vectors in $\mathbf{X}^{(2)}$ which is defined by (3.8). A straightforward calculation gives,

$$(J||Q||J) = (J||J||J)\{\tfrac{1}{6}(2J-1)(2J+3)\}^{1/2}.$$

It is to be noted that, the reduced matrix element of $\mathbf{Q}$ vanishes for $J = 1/2$, as expected in the light of the fact that for this value of J the operator $J_a^2 = 1/4$.

Our expression for $\langle Z\rangle_0$ to be used in (3.5) is $(\bar{l} = l - 1)$,

$$\langle Z\rangle_0 = \langle l|\, R|\bar{l}\rangle^2 \left\{ \frac{1}{3} n_h \frac{l}{(2l+1)} - \frac{P_2 \hat{\mathbf{q}}.\langle \mathbf{L}\rangle}{2(2l+1)} - E_0(\theta J)\langle \mathbf{Q}\rangle.\left\|\mathbf{X}^{(2)}\right\| \right\} . \qquad (4.1)$$

Here, $\hat{\mathbf{q}}$ is a unit vector in the direction of propagation of the beam and,

$$\left\langle l\left|R\right|\bar{l}\right\rangle^2 E_0(\theta J) = \sqrt{6}E(\theta J;\theta J)/(J\|Q\|J) ,$$

and $E(\theta J;\theta J)$ is obtained from (3.6).

Let us comment on each term on the right hand side of (4.1). The first term , often described as the isotropic term (apart from a factor 3), stems directly from $C(\theta J;\theta J)$. The value of $(\varepsilon'.\varepsilon)$ for a forward geometry is independent of the state of polarization in the primary beam, and has the value one; this and other combinations of polarization vectors needed to construct (4.1) are gathered in table 3. As with the other two terms in (4.1), we have factored out in (4.1) the square of the radial integral contained in C. The second term in (4.1), proportional to the mean helicity in the primary beam of X-rays, P_2, is derived from $D(\theta J;\theta J)$ and the relation $\mathbf{L} = (2 - g)\mathbf{J}$, where g is the Landé factor. The first two terms in (4.1) are the same for the *jj*-coupling and Russell-Saunders coupling schemes. (For a given configuration of the valence electrons, the numerical value of g depends on the coupling scheme employed.) The similarity in results for the two coupling schemes falters if the ground state wave function contains more than one value of J and the values include J and $J \pm 1$, for then there are off-diagonal contributions in D in Russell-Saunders coupling and the gyromagnetic factor is not given by the formula of Landé.

In the third, and last, term $E_0(\theta J)$ has a value which depends on the coupling scheme. A notation of vertical double bars around $\mathbf{X}^{(2)}$ denotes an average of the polarization vectors with respect to the of polarization in the primary beam, described by a Stokes vector $\mathbf{P} = (0, P_2, P_3)$; our definition follows the one used in reference [1]. Referring to table 3 we find that $\|\mathbf{X}^{(2)}\|$ does not depend on the mean helicity. The full

expression required in (4.1), written in terms of Cartesian components of ε, ε' and **J** in the set of axes labelled (a,b,c) is,

$$\begin{aligned}\langle \mathbf{Q} \rangle . \left\| \mathbf{X}^{(2)} \right\| = \tfrac{1}{2} \Big\{ & \left\langle J_c^2 - \tfrac{1}{3} J(J+1) \right\rangle \left\| 3\varepsilon_c' \varepsilon_c - \varepsilon' . \varepsilon \right\| \\ & + \left\langle J_b J_c + J_c J_b \right\rangle \left\| \varepsilon_b' \varepsilon_c + \varepsilon_c' \varepsilon_b \right\| + \left\langle J_a J_c + J_c J_a \right\rangle \left\| \varepsilon_a' \varepsilon_c + \varepsilon_c' \varepsilon_a \right\| \\ & + \left\langle J_a^2 - J_b^2 \right\rangle \left\| \varepsilon_a' \varepsilon_a - \varepsilon_b' \varepsilon_b \right\| + \left\langle J_a J_b + J_b J_a \right\rangle \left\| \varepsilon_a' \varepsilon_b + \varepsilon_b' \varepsilon_a \right\| \Big\} \ . \end{aligned} \tag{4.2}$$

The angular momentum operators in (4.2) arise in combinations which are Hermitian, so the thermal average values are purely real quantities. Values of the combinations of polarization vectors in (4.2) averaged over states of the primary polarization, **P**, are listed in table 3 where they are expressed in terms of Euler angles that relate the axes attached to the experimental geometry (x,y,z) and the quantization axes (a,b,c); relevant details about the Euler angles are listed in table 4. After averaging over all possible directions of the axis of quantization for the magnetic state of the atom, to create a condition of spherical symmetry, all terms in $\mathbf{X}^{(2)}$ vanish, as does the corresponding average of $\mathbf{X}^{(1)}$, of course. By way of another example, consider the case $\beta = 0$, for which the axes z and c coincide and the rotation of a and b relative to x and y is the angle $(\alpha + \gamma) = \delta$, say. In this special case, we find from (4.2) and entries in table 3,

$$\begin{aligned}\langle \mathbf{Q} \rangle . \left\| \mathbf{X}^{(2)} \right\| = \tfrac{1}{4} \Big\{ & \left\langle J_c^2 - \tfrac{1}{3} J(J+1) \right\rangle (1 + 3P_3) \\ & + (1 - P_3) \left[\left\langle J_a^2 - J_b^2 \right\rangle \cos 2\delta \ - \ \left\langle J_a J_b + J_b J_a \right\rangle \sin 2\delta \right] \Big\} \ . \end{aligned} \tag{4.3}$$

It is interesting to note from (4.3) that, for $\beta = 0$ and $P_3 = 1$ it is not possible to observe the terms which describe departures from cylindrical symmetry about the c-axis. A second example of interest is to align the axis of quantization and the direction of propagation of the beam of X-rays, achieved on setting $\alpha = \beta = (\pi / 2)$. One finds,

$$\langle \mathbf{Q} \rangle . \left\| \mathbf{X}^{(2)} \right\| = \tfrac{1}{2} \left\{ \left\langle \tfrac{1}{3} J(J+1) - J_c^2 \right\rangle \right. \tag{4.4}$$

$$\left. + P_3 \left[\left\langle J_a^2 - J_b^2 \right\rangle \cos 2\gamma \; - \; \left\langle J_a J_b + J_b J_a \right\rangle \sin 2\gamma \right] \right\} .$$

For the experimental geometry to which (4.4) applies, the attenuation coefficient is independent of the linear polarization described by P_3 if the atom has a cylindrical, or higher, magnetic symmetry.

The thermal average values of the operators in (4.1) - (4.4) are evaluated for the appropriate magnetic state of the absorbing atom. In the paramagnetic phase $\langle \mathbf{J} \rangle = 0$. The corresponding values of products of Cartesian components of **J**, in (4.2), (4.3) and (4.4), can have trivial values, e.g. in a truly isotropic environment all cross products, e.g. $\langle J_a J_b \rangle$, are zero, and the diagonal terms are all equal and have the value $J(J+1)/3$. Using these results in (4.2) one finds that all terms vanish. Hence, for a spatially isotropic environment the only contribution to $\langle Z \rangle_0$ which does not vanish is the first term on the right hand side of (4.1), proportional to the number of holes in the valence shell. Another simple case is when the environment has cylindrical symmetry about the *c*-axis. In this case all terms in (4.2) vanish apart from $\langle J_c^2 - J(J+1)/3 \rangle$. If the *c*-axis is singled out by a magnetic energy = $-B(J_c)^2$, the result,

$$\left\langle J_c^2 - \tfrac{1}{3} J(J+1) \right\rangle = \left(\frac{B}{T} \right) \frac{1}{45} J(J+1)(2J-1)(2J+3) ,$$

is correct to first order in (B/T), where T is the temperature in units of Boltzmann's constant. Magnetic order is induced by a Heisenberg interaction between the spin moments $(g-1)\mathbf{J}(\mathbf{R}_0)$. If this interaction is isotropic and treated within the mean-field approximation one finds $\langle J_c^2 \rangle = J^2$ at $T = 0$, and $\langle J_c^2 \rangle$ decreases with increasing temperature to the value $J(J+1)/3$ at the ordering temperature. More results for a molecular field model are found in reference [1].

As a final topic in this section, we consider so-called sum rules for the dichroic signal. If we integrate the attenuation coefficient (3.5) with respect to E in the vicinity of Δ the signal so obtained is proportional to $\langle Z \rangle_0$ which carries all available information about the physical properties of the absorbing atom. Ratios of $\langle Z \rangle_0$ for different settings of the polarization in the primary beam of X-rays are called normalized sum-rules of the dichroic signal. In $\mathbf{P} = (0, P_2, P_3)$ keep the magnitudes of P_2 and P_3 fixed and reverse the sign of P_2, the mean helicity. The difference in the signals is,

$$\langle Z(P_2) \rangle_0 - \langle Z(-P_2) \rangle_0 = - \langle l | R | \bar{l} \rangle^2 P_2 \, \hat{\mathbf{q}}.\langle \mathbf{L} \rangle / (2l+1) \; . \tag{4.5}$$

which, apart from some constants, is a result given in [9]. The expression for the difference signal is quite simple and has a strong physical appeal. However, this expression is derived from the mean value of Z within a single J-manifold which is not likely to be strictly accurate. Thole et al. [11] normalized the difference signal by the isotropic signal, defined to be three times the isotropic contribution to $\langle Z \rangle_0$ given by (4.1), and their normalized sum rule, for circular dichroism, is thus,

$$\frac{\{\langle Z(P_2) \rangle_0 - \langle Z(-P_2) \rangle_0\}}{\langle l | R | \bar{l} \rangle^2 n_h \{l/(2l+1)\}} = \frac{-P_2 \, \hat{\mathbf{q}}.\langle \mathbf{L} \rangle}{n_h l} \; . \tag{4.6}$$

Note that our derivation of the sum rule holds for both *jj*-coupling and Russell-Saunders coupling schemes. The result (4.6) has been obtained by a number of authors, using various mathematical methods of varying degrees of opacity; see [1,12], and references therein. In the present setting, the point to note is that the derivation of the normalized sum rule reported in [11] is also made without approximations, for an atomic model of the kind employed here. So, we deduce that the idealized scattering length we put forward embodies the same physical picture as the one used by Thole et al. To summarize, our idealized scattering length gives the correct value for the normalized, circular dichroic sum-rule, and, as a bonus, the truth

of the sum-rule is almost obvious to the eye. Set against this, the idealized scattering length, and the value for $\langle Z \rangle_0$ obtained from it, cannot answer questions about integrated signals associated with partners to a core edge [12].

§5 Resonance-enhanced Bragg diffraction

The value of the scattering length which describes Bragg diffraction is its mean value, averaged with respect to all atomic variables. We denote this scattering length by $\langle f \rangle$, where, as in previous sections, angular brackets denote a thermal average is made of the enclosed quantity. The cross-section for Bragg diffraction is proportional to,

$$\sigma = \left\| \left| \langle f \rangle \right|^2 \right\| , \tag{5.1}$$

where the double vertical bars denote an average with respect to the states of polarization in the primary beam. While a realistic wave function for the ground state of an open valence shell is likely to contain various contributions, with different values of θ and J, by way of orientation, we evaluate the mean scattering length for a pure state which contains one set of values for θ and J, and possibly several values of the magnetic quantum number. For this very special type of ground state, we can use the operator equivalents introduced in the previous section.

From (3.3) evaluated for $E = \Delta$, one finds,

$$\langle f \rangle = \left(\frac{2i}{\Gamma}\right)\left(\frac{2\pi e}{\lambda}\right)^2 \sum_{\mathbf{R}_0} \exp(i\mathbf{k}.\mathbf{R}_0) \langle Z(\mu;\mu:\mathbf{R}_0) \rangle \ . \tag{5.2}$$

The result,

$$\langle Z(\mu;\mu{:}\mathbf{R}_0)\rangle = \langle l|R|\bar{l}\rangle^2 \left\{ \frac{1}{3} n_h \frac{l}{(2l+1)} (\boldsymbol{\varepsilon}'.\boldsymbol{\varepsilon}) + \mathrm{i} \frac{\langle \mathbf{L} \rangle .(\boldsymbol{\varepsilon}' \times \boldsymbol{\varepsilon})}{2(2l+1)} - E_0 \langle \mathbf{Q} \rangle . \mathbf{X}^{(2)} \right\}, \quad (5.3)$$

follows directly from (3.11). The function E_0 appears also in (4.1) and it is proportional to $E(\theta J;\theta J)$. The explicit form of the coefficient of E_0 in (5.3) is readily deduced from (4.2). The dependence of $\langle Z \rangle$ on the position of the atom, $\mathbf{R}_0$, arises from the dependence of the atomic variables $\langle \mathbf{L} \rangle$ and $\langle \mathbf{Q} \rangle$ on the axes of quantization (a, b, c) used to calculate the magnetic properties of the atom at site $\mathbf{R}_0$.

The condition on $\mathbf{k}$ for Bragg diffraction arises from translational invariance of $\langle Z \rangle$ in a crystal. Let there be N unit cells, and denote the magnetic reciprocal lattice vectors by $\{\tau\}$; then,

$$\langle f \rangle = \frac{2\mathrm{i}}{\Gamma} \left(\frac{2\pi e}{\lambda} \right)^2 N \sum_{\tau} \delta_{\mathbf{k},\tau} F(\tau) \quad . \quad (5.4)$$

Here, the Kronecker delta function is unity if $\mathbf{k} = \tau$ and zero otherwise, and the magnetic unit cell structure factor,

$$F(\tau) = \sum_{\mathbf{d}} \exp(\mathrm{i}\tau.\mathbf{d}) \, \langle Z(\mu;\mu{:}\mathbf{d}) \rangle \, , \quad (5.5)$$

in which the r atoms in the cell are at positions defined by $(r - 1)$ non-null vectors $\{\mathbf{d}\}$. Work in [14] addresses the calculation of the unit cell structure factor for a variety of states of magnetic order.

Possibly the biggest headache in calculating the cross-section (5.1) is performing the average over the states of polarization in the primary beam of X-rays. At least, this is the case for a ferromagnet since, in this instance, all components in $\langle Z \rangle$ add coherently. In other examples of magnetic ordering the magnetic and non-magnetic components of $\langle Z \rangle$ might not add coherently and, in consequence, the

intensity of Bragg peaks can be assigned to pure magnetic or pure chemical order in the crystal.

To illustrate the structure which is possible in the cross-section for Bragg diffraction we consider a ferromagnetic component to $F(\tau)$, and reduce the complexity of $\langle Z \rangle$ to one consistent with magnetic cylindrical symmetry. The form of $F(\tau)$ is taken to be,

$$F(\tau) = A_1(\varepsilon'.\varepsilon) + iA_2\mathbf{m}.(\varepsilon' \times \varepsilon) + A_3(\varepsilon'.\mathbf{m})(\varepsilon.\mathbf{m}) \ , \tag{5.6}$$

where $\mathbf{m}$ is a unit vector that defines the preferred magnetic axis. The coefficient A_2 is simply read off by inspection of (5.3), and it is proportional to $|\langle \mathbf{L} \rangle|$. On the other hand, A_1 is a sum of the isotropic contribution to $\langle Z \rangle$ and the part of the coefficient of $\langle Q_c \rangle$ proportional to $(\varepsilon'.\varepsilon)$, and A_3 is the remaining part of this contribution, cf. (4.2). In the following expression for the average of the absolute square of (5.6), with respect to states of polarization described by a Stokes vector $\mathbf{P} = (0, P_2, P_3)$, we use the coordinate system for the geometry of the diffraction experiment which is the subject of entries in table 4. (The coordinate system we use is the same as the one described in reference [1], to which the reader is referred for details of the technique, based on a density matrix representation, for executing the average over states of polarization.) One obtains, for the unit cell structure factor (5.6), the result,

$$\begin{aligned} \left\| |F|^2 \right\| &= \tfrac{1}{2}(1+P_3)(A_1 + A_3 m_z^2)^2 + \tfrac{1}{2}(1-P_3)\left(A_1 \cos\theta + A_3(\varepsilon'_\pi.\mathbf{m})(\varepsilon_\pi.\mathbf{m})\right)^2 \\ &+ A_2^2\left[(\mathbf{m}.\hat{\mathbf{q}}')^2 + (1-P_3)\sin\theta\left(\tfrac{1}{2}m_z^2\sin\theta - m_x m_y\right)\right] \\ &+ A_3^2 m_z^2\left[(\mathbf{m}.\varepsilon'_\pi)^2 + (1-P_3)m_x m_y \sin\theta\right] \\ &- P_2 A_2\left[A_1\mathbf{m}.(\hat{\mathbf{q}} + \hat{\mathbf{q}}'\cos\theta) + A_3(\mathbf{m}.\hat{\mathbf{q}}')\left(m_z^2\cos\theta + (\varepsilon'_\pi.\mathbf{m})(\varepsilon_\pi.\mathbf{m})\right)\right] . \end{aligned} \tag{5.7}$$

Here, m_X, m_Y, and m_Z are the components of the unit vector $\mathbf{m}$ along the axes (x, y, z), and A_1, A_2, and A_3 are taken to be purely real quantities. The foregoing result can be

manipulated to a variety of equivalent forms. The form chosen in (5.7) has the advantage of clearly displaying the simplification which occurs at a diffractometer on a source of X-rays produced by a particle accelerator where $P_2 \cong 0$ and $P_3 \cong 1$, to a good approximation, is the standard setting.

A few features of the result (5.7) merit comment. If $P_3 = -1$ (NB $P_2^2 + P_3^2 \leq 1$) and the beam is deflected through $\theta = (\pi / 2)$ the cross-section is independent of A_1. With this setting, the cross-section depends on A_2 and A_3, and in the paramagnetic phase $A_2 = 0$, and $A_3 = 0$ for an isotropic environment. The term containing P_2, the mean helicity, is linear in A_2, as expected. If the components A_1 and A_3, and A_2 do not add coherently for the chosen value of τ then one has either to set in (5.7) $A_1 = A_3 = 0$ or $A_2 = 0$. For an isotropic paramagnet $A_2 = A_3 = 0$, and the right hand side of (5.7) reduces to the result obtained for Thomson scattering. For random orientations of **m**,

$$\left\| |F|^2 \right\| = (A_1 + \tfrac{1}{3} A_3)^2 + \tfrac{1}{3} A_2^2 + \tfrac{7}{45} A_3^2 \qquad (5.8)$$

$$+ \tfrac{1}{2}(1 - P_3)\sin^2\theta \left[\tfrac{1}{3} A_2^2 - (A_1 + \tfrac{1}{3} A_3)^2 - \tfrac{1}{45} A_3^2 \right].$$

Note that (5.8) does not depend on P_2 or the sign of A_2, which is to be expected, of course. Lastly, we choose for the Stokes parameters the extreme values $P_2 = 0$ and $P_3 = 1$, which describes a state of complete polarization perpendicular to the plane of scattering;

$$\left\| |F|^2 \right\| = A_1^2 + 2A_1 A_3 m_z^2 + A_2^2 (\mathbf{m}.\hat{\mathbf{q}}')^2 + \left(A_3 m_z\right)^2 \left\{ 1 - (\mathbf{m}.\hat{\mathbf{q}}')^2 \right\}. \qquad (5.9)$$

It is interesting to note that there is an interference between the components A_1 and A_3, of the structure factor, which vanishes if the moment lies in the plane of scattering, and $m_z = 0$.

§6 Resonance-enhanced inelastic scattering

The differential cross-section for resonance-enhanced inelastic scattering by one atom is,

$$\left(\frac{d\sigma}{dE'}\right) = \left(\frac{E'}{E}\right)\sum_{\mu\mu'} p_\mu \, \delta\left(\hbar\omega + E_\mu - E_{\mu'}\right) \left\| \left| f(\mu;\mu') \right|^2 \right\| . \qquad (6.1)$$

This result is independent of the scattering wave vector. We have defined $\hbar\omega = E - E'$, and the conservation of energy leads to $E' = \Delta'$ for $E = \Delta$. Hence, the scattering length to appear in (6.1), at the condition of resonance, is,

$$f(\mu;\mu') = \left(\frac{2i}{\Gamma}\right)\left(\frac{2\pi e}{\lambda}\right)^2\left(\frac{E'}{E}\right) Z(\mu;\mu') . \qquad (6.2)$$

In (6.1) there is a sum over all final states, and an average over all the initial states weighted by p_μ, and the sum over p_μ is normalized to unity.

The features of inelastic events depend on the coupling scheme for angular momenta. Let us start by considering the *jj*-coupling scheme. For $n_h = 1$ and $n_h = 2j$ one replaces T by t whose reduced matrix element is given by (A.5). Inelastic transitions are between states with total angular momentum j and j', and proceed via the tensors with $K = 1$ and 2 in D and E, respectively. The appropriate expression for D is (6.4), whereas (3.7) applies to elastic events ($j = j'$) for $n_h = 1$ and $n_h = 2j$, and elastic and inelastic events for n_h equivalent holes and $2 \le n_h \le (2j-1)$. The quantity E is obtained from the expression given in (3.6) evaluated with the appropriate value of the reduced matrix element of $T(2)$, i.e. the result in (A.5) and $K = 2$.

Non-equivalent particles are handled by techniques described in reference [4]. Here, we consider the case of two particles, which is of interest in studies of some

actinide atoms. Let the states j^2 and (jj') have total angular momentum J, and J', respectively, and set $j \neq j'$. The allowed J are restricted to the even integer values 0,2,...$(2j - 1)$, cf. (A.9), whereas J' merely satisfies the triangle conditions $|j - j'| \leq J' \leq (j + j')$ and, as we will see, $|J - K| \leq J' \leq (J + K)$. The reduced matrix element of $T(K)$ needed in (A.4) is,

$$\left(J\|T(K)\|J'\right) = \left(j\|t(K)\|j'\right)\sqrt{2}(-1)^{K+j+j'}\left\{(2J+1)(2J'+1)\right\}^{1/2}\begin{Bmatrix} J & K & J' \\ j' & j & j \end{Bmatrix}. \quad (6.3)$$

The phase factor in (6.3) is for a state (jj') with angular momentum J', and it is different for the state ordered $(j'j)$. Also, for $j \neq j'$ the event $j^2 \rightarrow j'^2$ is forbidden with a one particle operator. The value for E is obtained by using (6.3) in the expression given in (3.6). However, the value for D is,

$$D = \frac{1}{2}\left\{\frac{l(l+1)}{(2l+1)}\right\}^{1/2}\left(J\|T(1)\|J'\right)\left\langle l|R|\bar{l}\right\rangle^2, \quad (6.4)$$

which reduces to the expression for two or more equivalent holes given in (3.7) when the appropriate value is taken for the reduced matrix element, viz. (A.10) and (A.12). For non-equivalent particles the quantity D is not diagonal with respect to J, and $J' = J$ and $J' = J \pm 1$. (NB The same conditions hold for $n_h = 1$ and $n_h = 2j$, with $J = j$ and $J' = j'$.)

Returning to the case of n equivalent particles, it remains to consider the case $2 \leq n_h \leq (2j - 1)$. Inspection of the results for C and D in (3.7) show that they are diagonal with respect to J. So, in the jj-coupling scheme, transitions between states with $J \neq J'$ can only proceed via E, and the selection rule is $J' = J \pm 1$, and $J' = J \pm 2$. As we noted, transitions via D, in addition to E, are allowed for $n_h = 1$ or $n_h = 2j$.

In the Russell-Saunders scheme D is diagonal with respect to $\theta \equiv \nu SL$. Hence, this term contributes to transitions with $J' = J \pm 1$ provided the initial and final states of the valence shell are in the same multiplet. Looking at E one finds it is diagonal with respect to S, and the selection rule on transitions is $J' = J \pm 1$, and $J' = J \pm 2$.

By way of an orientation to the magnitude of inelastic events in resonance-enhanced scattering we consider transitions between two states each completely described by one set of labels θJ. In addition, we assume the spread in energy of states with respect to the magnetic quantum numbers is too small to resolve in an experiment. The appropriate cross-section is proportional to $|Z(\mu;\mu')|^2$, with $\mu = \theta JM$ and $\mu' = \theta' J' M'$, summed over M', and summed over M with a degeneracy factor $1/(2J+1)$. If $J \neq J'$ there is no contribution to the cross-section from C, since it is diagonal in this quantum number. We obtain the result,

$$\sum_{MM'} \frac{1}{(2J+1)} |Z(\mu;\mu')|^2 = \frac{1}{(2J+1)} \left\{ \tfrac{2}{3} D^2 \left|\mathbf{X}^{(1)}\right|^2 + \tfrac{6}{5} E^2 \left|\mathbf{X}^{(2)}\right|^2 \right\} . \qquad (6.5)$$

Note that there is no term in DE. Also, $\left|\mathbf{X}^{(1)}\right|^2 = \frac{1}{2}(\varepsilon' \times \varepsilon).(\varepsilon' \times \varepsilon)$, and if we set aside the influence of a partial polarization of the primary beam,

$$\left\| \left|\mathbf{X}^{(1)}\right|^2 \right\| = \tfrac{1}{4}(2 + \sin^2\theta) ,$$

together with,

$$\left\| \left|\mathbf{X}^{(2)}\right|^2 \right\| = \tfrac{1}{12}(13 + \cos^2\theta) .$$

In these two expressions, θ is the angle through which the secondary beam is deflected relative to the direction of the primary beam. The value of $\left|\mathbf{X}^{(1)}\right|^2$ averaged with respect to states of partial polarization in the primary beam is found in reference [1].

Turning to the question of the magnitude of inelastic events we first consider a few numbers for a configuration f^{12} and a Russell-Saunders ground state $^3H_6$, which is a zeroth-order model for thulium. Both D and E contribute in the transition to $^3H_5$, and we find,

$$D(^3H_6;^3H_5) = -\ 0.235\ \langle l|R|\bar{l}\rangle^2\ ,$$

$$E(^3H_6;^3H_5) = -\ 0.096\ \langle l|R|\bar{l}\rangle^2\ .$$

Relative to the weight of the elastic event the inelastic contribution from D is quite significant, namely,

$$\frac{D(^3H_6;^3H_5)}{D(^3H_6;^3H_6)} = -\ 0.169\ .$$

Transitions to $^3H_4$ and $^3F_4$ can only proceed through E, and we find,

$$E(^3H_6;^3H_4) = -\ 0.132\ E(^3H_6;^3H_5)\ ,$$

and,

$$E(^3H_6;^3F_4) = \ 0.266\ \langle l|R|\bar{l}\rangle^2\ .$$

To conclude, we give some of the corresponding values for f^2 treated within the jj-coupling scheme. For $j = \frac{5}{2}$ and $J = 4$, the elastic value of the quantity D is,

$$D(4;4) = 1.095\ \langle l|R|\bar{l}\rangle^2\ ,$$

which is now compared to values for D and E calculated for transitions to the states of the configuration $\left(\frac{7}{2},\frac{5}{2}\right)$, and derived from (6.3). We choose $J' = 4$ and find,

$$D(j^2 4; j'j4) = -0.102 \left\langle l|R|\bar{l}\right\rangle^2 ,$$

and,

$$E(j^2 4; j'j4) = -0.104 \left\langle l|R|\bar{l}\right\rangle^2 .$$

So, once more, the weight available for inelastic transitions is only an order of magnitude smaller than for the elastic contribution. Transitions within a j^n configuration can only be made via E, since C and D are diagonal with respect to J, and transitions between the j = 5/2 and 7/2 states of equivalent electrons are forbidden.

§7 Summary

A formulation of the absorption and resonance-enhanced scattering of X-rays by a magnetic material is put forward. Its main virtue is seen to lie in the possibility for greater use to be made of physical intuition at an atomic level of detail. The scattering length, common to absorption and resonance-enhanced scattering, in the proposed interpretation is built of quantities related to the equilibrium configuration of the atoms, and also obtainable from the interpretation of empirical data gathered using other techniques, firmly established as valuable quantitative tools of investigation, e.g. NMR, Mossbauer spectroscopy and the scattering of beams of neutrons.

The formulation which is proposed lies between two extreme approaches to the calculation of the scattering length. On the one hand, all variables relating to the virtual, intermediate states in the scattering length can be removed by completely ignoring the structure in the energy spectrum of the intermediate states followed by the use of the closure relation for the states. In this extreme, the scattering length is independent of the magnetic moment of the atom; all the magnetic information that

remains relates to even-order moments of the valence electrons. The other extreme is to calculate all the wave functions and energies of the intermediate states and the matrix elements which appear in the scattering length. This task demands the resource of a tried and tested computer program for atomic structure, for all but the simplest case of one hole in the valence shell. Most importantly, though, it is difficult in this case to directly relate the calculated scattering length to quantities of interest, to wit, quantities which arise in the interpretation of potentially complementary experiments and theoretical developments in magnetism. In this framework of reasoning, the scattering length we have proposed imposes a coarsened resolution to the structure in the spectrum of intermediate states, and does not discriminate between spin-orbit split partners in an absorption edge. Set against this, with the less than perfect resolution applied to the intermediate states, the scattering length is still sensitive to the magnetic moment and this, and all other atomic contributions, are immediately recognizable in the formulation. Whether or not the coarsening can be tolerated in applications depends on several factors, among them being the objectives in the experimental investigation, the indigenous broadening of the level structure of the intermediate states, and the resolution applied in the experiments.

The new theory has been investigated using both *jj*-coupling and Russell-Saunders coupling schemes. Measurable quantities calculated are the attenuation coefficient, and cross-sections for resonance-enhanced Bragg diffraction and inelastic scattering, including their dependence on states of partial polarization in the primary beam.

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Appendix A

In the derivation of the idealized scattering length for a multi-electron occupation of a valence shell with angular momentum l we start from an exact formula for the product of matrix elements in the scattering length, (2.1) together with (2.2), which is correct for one particle in the valence shell. We work with the dipole approximation to the current operator. However, the method we describe can be applied to higher-order multipole operators; the final formulae are even more cumbersome than for dipole-allowed transitions, as might be anticipated.

The dipole operator for one particle $R_q = RC^1_q(\hat{\mathbf{R}})$ where $q = -1, 0, +1$ labels spherical components of the position variable, and $C^1_q(\hat{\mathbf{R}})$ is a spherical harmonic of rank one, normalized in the manner proposed by Racah. A matrix element of R_q satisfies the Wigner-Eckart theorem (3.1). The reduced matrix element of R_q involves the coupling of three angular momenta and the appearance of a 6j-symbol is thus anticipated. The result is,

$$\left(lJ\|R\|\bar{l}\bar{J}\right) = (-1)^{3/2-J+l}\left\langle l|R|\bar{l}\right\rangle\left(l\|C(1)\|\bar{l}\right)\ \left[(2J+1)(2\bar{J}+1)\right]^{1/2}\begin{Bmatrix} J & 1 & \bar{J} \\ \bar{l} & \frac{1}{2} & l \end{Bmatrix}. \qquad \text{(A.1)}$$

Here,

$$\left(l\|C(1)\|\bar{l}\right) = (-1)^{l}\ \left[(2l+1)(2\bar{l}+1)\right]^{1/2}\begin{pmatrix} l & 1 & \bar{l} \\ 0 & 0 & 0 \end{pmatrix}, \qquad \text{(A.2)}$$

and the 3j-symbol vanishes if $l+1+\bar{l}$ is an odd integer. The latter result and the triangular condition leads to the dipole selection rule; all terms which do not satisfy $\bar{l} = l \pm 1$ are zero. In (A.1) there is also the radial matrix element of order one for the valence and core wave functions. As an illustration of the value of this matrix element we refer to the values for 4d-4f absorption in the lanthanides given in reference [6], where it is found that the average for the charge states 63 through to 67 is – 0.63 in units of the Bohr radius.

The product of matrix elements which appears, together with other quantities, in the formula for our idealized scattering length is,

$$\sum_{\bar{J}\bar{M}} \left\langle lJM \middle| R_q \middle| \bar{l}\ \bar{J}\ \bar{M} \right\rangle \left\langle \bar{l}\ \bar{J}\ \bar{M} \middle| R_{q'} \middle| lJ'M' \right\rangle. \tag{A.3}$$

Each matrix element is obtained from the Wigner-Eckart theorem (3.1) and (A.1). Hence, the nub of the calculation we face is to perform the sum over $\bar{J}$ and $\bar{M}$ of a product of four nj-symbols; two 3j-symbols, which come from the Wigner-Eckart theorem and contain both $\bar{J}$ and $\bar{M}$ in their arguments, and two 6j-symbols which depend on $\bar{J}$. A method of performing the sum over $\bar{J}$ and $\bar{M}$ is to use an identity for the product of two 6j-symbols that expresses them as a sum of the product of three 6j-symbols, a step forward because $\bar{J}$ occurs in just one of the three 6j-symbols. The calculation, then, requires the sum over $\bar{J}$ and $\bar{M}$ of the product of two 3j-symbols and one 6j-symbol; the answer is a product of two 3j-symbols, one of which has as arguments the quantities demanded by the Wigner-Eckart theorem. The two identities we have referred to in the outline of the calculation defined in (A.3) can be found in the book by Rotenberg et al. [15], equations (2.8) and (2.19).

The physical process we need to describe is the transfer of one hole from the valence shell to a core state full of electrons. Of course, the occupation of the valence shell, in its ground state configuration, strongly influences the process. An extreme is

a valence shell full of electrons, and no holes, $n_h = 0$. In this case, the process of interest is forbidden. Our result, just described, for the quantity defined in (A.3), correctly describes the process for a valence shell whose ground state configuration contains one hole, $n_h = 1$. It is now generalized to a configuration $n_h > 1$ by a straightforward application of the method, due to Racah, which uses fractional parentage coefficients to describe a state of n_h equivalent particles. It is necessary to give some thought to the use of the method to a configuration of holes, in contrast to the more familiar example of electrons; not surprisingly, answers to the relevant points of concern are given by Racah; see §6 of reference [16].

All the formulae we need for fractional parentage coefficients, for *jj*- and Russell-Saunders coupling, are contained in the book by de-Shalit and Talmi [4]. (NB the identity in Rotenberg et al. numbered (2.19) is reproduced by de-Shalit and Talmi, equation (15.14), but the printed formula contains a misprint.) The result for (A.3) that applies for $n_h \geq 1$ equivalent holes we denote by Υ and its value is,

$$\Upsilon_{qq'}(\theta JM;\theta' J'M') = \sum_{K,m_0} \left\langle \theta JM \middle| T^K_{m_0} \middle| \theta' J'M' \right\rangle (-1)^{m_0} \qquad \text{(A.4)}$$

$$\times (2K+1)(l\|C(1)\|\bar{l})\,(\bar{l}\|C(1)\|l)\left\langle l|R|\bar{l}\right\rangle^2 \begin{Bmatrix} 1 & K & 1 \\ l & \bar{l} & l \end{Bmatrix} \begin{pmatrix} 1 & K & 1 \\ q & -m_0 & q' \end{pmatrix}.$$

The matrix element of the tensor $T^K_{m_0}$ satisfies (3.1), and $m_0 = M - M' = q + q'$. The triangular condition on K limits its values to 0, 1 and 2. The label θ, about which we have more to say later in the appendix, is a composite label that denotes all the quantum numbers required to uniquely define a state over and above the labels (quantum numbers) J and M. All quantities in (A.4) are dimensionless apart from the radial integral, and Υ has the dimension of (length)^2. No approximation is made in reaching the result (A.4) for the quantity defined by (A.3), as hopefully, is clear from the derivation which is described.

The value of the reduced matrix element of T which arises in (A.4) on application of the Wigner-Eckart theorem (3.1) depends on the coupling scheme. We

start with the *jj*-coupling scheme. For this scheme, θ is the seniority quantum number [4]; it is often denoted by ν and we henceforth comply with this convention. For one particle $T = t$ and a building block in the reduced matrix element of T for $n_h \geq 2$ particles is the reduced matrix element of t. Let $j = l \pm ½$; one finds,

$$(j\|t(K)\|j') = (-1)^{j+K+\frac{1}{2}+l}\left[(2j+1)(2j'+1)\right]^{\frac{1}{2}}\begin{Bmatrix} j & K & j' \\ l & \frac{1}{2} & l \end{Bmatrix}. \qquad \text{(A.5)}$$

The phase factor in (A.5) is for the scheme in which spin is coupled to orbital angular momentum, i.e. the Clebsch-Gordan coefficient in the coupling is $(½\ m_s\ lm|jm_j)$. (If the spin and orbital angular momentum labels are reversed in the Clebsch-Gordan coefficient a different phase factor is obtained in the corresponding reduced matrix element of t. Two well-known texts on atomic theory use different coupling schemes. Judd [17] and the present work concur and use the *SL*-scheme, adopted by Racah, and Cowan [18] uses the *LS*-scheme. In their book on nuclear shell theory, de-Shalit and Talmi [4] use the *SL*-scheme.) For the configuration of n_h equivalent particles, j^{n_h}, T is the sum of n_h ts and the reduced matrix element is,

$$\left(\nu J\|T(K)\|\nu' J'\right) = \left(j\|t(K)\|j\right)(2K+1)^{-\frac{1}{2}}\left(\nu J\|V(K)\|\nu' J'\right). \qquad \text{(A.6)}$$

It is noted in (A.6) that on the right hand side the reduced matrix element of t is evaluated for $j = j'$. The reduced matrix element of V is compiled from fractional parentage coefficients and 6j-symbols; our definition of the reduced matrix element and various properties of magnetic atoms described by a *jj*-coupling scheme, are found in [10]. Table 1a lists values of interest in the study of magnetic materials. The following properties of the reduced matrix elements of V are to be noted.

For $K = 0$, the reduced matrix element of V vanishes unless $J = J'$ and $\nu = \nu'$:

$$\left(\nu J\|V(0)\|\nu' J'\right) = n_h\left(\frac{2J+1}{2j+1}\right)^{1/2}\delta_{J,J'}\delta_{\nu,\nu'}\ , \qquad \text{(A.7)}$$

Reduced matrix elements with K odd have the remarkable property of being independent of the numbers of particles, and diagonal with respect to the seniority number. For our purposes we need only one case, namely,

$$\left(vJ\|V(1)\|v'J'\right) = \sqrt{3}\,\frac{(J\|J\|J)}{(j\|j\|j)}\delta_{J,J'}\delta_{v,v'}\,, \tag{A.8}$$

where $(j\|j\|j)^2 = j(j+1)(2j+1)$. For $n_h = 2$ the reduced matrix element vanishes unless J and J' are even integers, in which case, for all K,

$$\left(vJ\|V(K)\|v'J'\right) = 2\delta_{v,v'}\left[(2J+1)(2K+1)(2J'+1)\right]^{1/2}(-1)^{2j+K}\begin{Bmatrix} J & K & J' \\ j & j & j \end{Bmatrix}. \tag{A.9}$$

For K = even integer, $K \geq 2$, and $v = v'$:

$$\left(j^n vJ\|V(K)\|j^n vJ'\right) = \left(\frac{2j+1-2n}{2j+1-2v}\right)\left(j^v vJ\|V(K)\|j^v vJ'\right),$$

For K = even integer, $K \geq 2$, and $v' = v-2$:

$$\left(j^n vJ\|V(K)\|j^n v-2J'\right) = \left(\frac{(n-v+2)(2j+3-n-v)}{2(2j+3-2v)}\right)^{1/2}\left(j^v vJ\|V(K)\|j^v v-2J'\right).$$

It is interesting to observe that the coefficients in these two results for K an even integer are obtained from corresponding θ-basis relations, to be given, by using, $j \to 2l+1/2$, i.e. $2j+1 \leftrightarrow 2(2l+1)$.

The state j^n and its conjugate state j^{2j+1-n} have the same quantum numbers, including the seniority. From the foregoing it is evident that, for the conjugate state:

- an odd tensor has the same sign and magnitude as the state j^{n_h},

and,

- an even tensor ($K \geq 2$) for

$v = v'$: has same magnitude and opposite sign

$v' = v - 2$: has same magnitude and sign.

It is interesting to observe that the scattering of neutrons by a magnetic atom is described entirely by reduced matrix elements of $V(K)$ with $K = 1, 3, \ldots$[10].

The matrix elements for configurations of non-equivalent holes are provided by de-Shalit and Talmi [4]. We give one example in §6.

Let us survey the behaviour of the reduced matrix element of $V(K)$ as a function of the number of particles (holes) n_h. For $n_h = 0$ the reduced matrix element for all values of K has the value zero. This statement is obviously correct for $K = 0$ because the matrix element (A.7) is proportional to n_h. For other values of K the reduced matrix element is zero when the quantum numbers are given values appropriate for $n_h = 0$, namely, $L = L' = S = S' = J = J' = 0$. By the same argument, all the reduced matrix elements for $K > 0$ are zero for the maximum number of holes, $n_h = (2j+1)$. The physical content of this result is that, for $n_h = (2j+1)$ the valence shell is spherically symmetric and, hence, unable to carry information about the environment. By definition, for $n_h = 1$,

$$(vj||V(K)||vj) = (2K+1)^{1/2} \; ; \quad \text{all } K.$$

The corresponding result for the conjugate state, $n_h = 2j$, applies for $K > 0$ — the result for $K = 0$ is (A.7) — and it is,

$$(vj||V(K)||vj) = (-1)^{1+K}(2K+1)^{1/2} \; .$$

The other coupling scheme of interest in the study of magnetic materials is the *SL*-coupling, or Russell-Saunders scheme. In this scheme, θ is an abbreviation for the three quantum numbers *v*, *S*, and *L*. For the reduced matrix element of *T* one finds,

$$\left(\theta J\|T(K)\|\theta' J'\right) = \delta_{s,s'}(-1)^{L'+J+S+K}\left[\frac{(2J+1)(2J'+1)}{(2K+1)}\right]^{1/2}\begin{Bmatrix} J' & L' & S \\ L & J & K \end{Bmatrix}(\theta\|V(K)\|\theta'). \tag{A.10}$$

Like its counterpart in *jj*-coupling, the reduced matrix element $(\theta\|V(K)\|\theta')$ is constructed from fractional parentage coefficients and 6j - symbols; our definition is identical with the one adopted by Judd [17], equation (7.52), however the author does not consider *jj*-coupling. In reference [4] both coupling schemes are considered. An extensive tabulation of reduced matrix elements is found in reference [19], part of which is here reproduced in table 1b.

Special cases of interest are,

$$\left(\theta\|V(0)\|\theta'\right) = n_h\,\delta_{\theta,\theta'}\left(\frac{2L+1}{2l+1}\right)^{1/2}, \tag{A.11}$$

and,

$$\left(\theta\|V(1)\|\theta'\right) = \sqrt{3}\,\delta_{\theta,\theta'}\,\frac{(L\|L\|L)}{(l\|l\|l)}. \tag{A.12}$$

For K = even integer and $v = v'$,

$$\left(l^n vSL\|V(K)\|l^n vS'L'\right) = \left(\frac{2l+1-n}{2l+1-v}\right)(l^v vSL\|V(K)\|l^v vS'L'),$$

and,

$$\left(l^n vSL\|V(K)\|l^n v-2,S'L'\right)=\frac{1}{2}\left(\frac{(n-v+2)(4l+4-n-v)}{(2l+2-v)}\right)^{1/2}(l^v vSL\|V(K)\|l^v v-2,S'L'),$$

The seniority selection rule is $v-v'=0,\pm 2$.

Matrix elements for a given state and its conjugate are the same for odd rank tensors, and of equal magnitude and opposite sign for even tensors.

The properties of the reduced matrix elements of $V(K)$ for $n_h = 0$ and 1 and the conjugate states that we noted earlier in the *jj*-coupling scheme have their counterparts in the Russell-Saunders coupling scheme. For $n_h = 0$ and $n_h = 2(2l+1)$, the reduced matrix elements with $K > 0$ are zero. For $n_h = 1$,

$$(l||V(K)||l)=(2K+1)^{1/2}\ ;\qquad \text{all } K,$$

and for $n_h = (4l+1)$, and $K > 0$,

$$(l||V(K)||l)=(-1)^{1+K}(2K+1)^{1/2}\ .$$

Values for $K = 0$ and all n_h are obtained from (A.12).

In the problem of describing the scattering of neutrons by a magnetic atom, with states represented in the *SL*-scheme, the interaction mediated by the current (often called the orbital interaction) is expressed in terms of the reduced matrix elements of V with an odd order. The second part of the interaction, arising from the dipolar interaction between the (spin) moment of the electron and the magnetic moment of the neutron, can not be expressed in terms of V, see reference [20]. In this respect, the description of neutron scattering by a magnetic atom depends on the type of coupling scheme used to classify its states, l^n.

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Table 1a

***jj*-coupling scheme:**

Total angular momentum and seniority numbers for the Hund's-rule ground states of tripositive lanthanides together with the number of electrons $n = 2j + 1 - n_h$. The last column gives the reduced matrix element of $V(2)$ for the ground state. Our definition of the reduced matrix element, in terms of fractional parentage coefficients, is given in reference [10]. All even rank tensors are zero for a half-filled closed shell, and for $n_h = 1$ the value of the reduced matrix element for all K is $(2K+1)^{1/2}$, and for $n_h = 2j$ it has the same magnitude and opposite sign. In the first (second) shell $j = \frac{5}{2}\left(\frac{7}{2}\right)$ and the Landé factor $g = \frac{6}{7}\left(\frac{8}{7}\right)$. The moment $\langle w^{101} \rangle$ in reference [7] is simply $(2-g)J/l$, and the same formula applies for the Russell-Saunders coupling using the appropriate value for g.

Configuration	J	n	v	$\left(vJ\|V(2)\|vJ\right)$
$j = 5/2$:				
Ce^{3+} f^1	$\frac{5}{2}$	1		$-\sqrt{5}$
Pr^{3+} f^2	4	2	2	$-\frac{1}{7}\sqrt{165}$
Nd^{3+} f^3	$\frac{9}{2}$	3	3	0
Pm^{3+} f^4	4	4	2	$\frac{1}{7}\sqrt{165}$
Sm^{3+} f^5	$\frac{5}{2}$	5		$\sqrt{5}$
Eu^{3+} f^6	0	6		0
$j = 7/2$:				
Gd^{3+} f^7	$\frac{7}{2}$	1		$-\sqrt{5}$
Tb^{3+} f^8	6	2	2	$-2\sqrt{\frac{65}{33}}$
Dy^{3+} f^9	$\frac{15}{2}$	3	3	$-\frac{1}{7}\sqrt{170}$
Ho^{3+} f^{10}	8	4	4	0
Er^{3+} f^{11}	$\frac{15}{2}$	5	3	$\frac{1}{7}\sqrt{170}$
Tm^{3+} f^{12}	6	6	2	$2\sqrt{\frac{65}{33}}$
Yb^{3+} f^{13}	$\frac{7}{2}$	7		$\sqrt{5}$

Table 1b

Russell-Saunders coupling scheme:

The value of the reduced matrix element of $V(2)$ for the ground state configuration of tripositive lanthanides derived from Hund's rules. The values for $V(2)$ are obtained from the tabulation of the reduced matrix elements of $U(2)$ found in reference [19] and the relation $V(K) = (2K+1)^{1/2} U(K)$. The reduced matrix element of $V(K)$ for a number of holes = $(14 - n_h)$ has the same magnitude and opposite sign to the value listed for the value n_h. For $n_h = 0$ and $n_h = 14$ the reduced matrix element of $V(2)$ is zero. The Landé factor is obtained from formula (2.83) in reference [1].

Ground state	n_h	$(\theta J \Vert V(2) \Vert \theta J)$
^2F	1	$\sqrt{5}$
^3H	2	$\frac{1}{3}\sqrt{\frac{715}{14}}$
^4I	3	$\sqrt{\frac{65}{66}}$
^5I	4	$-\sqrt{\frac{65}{66}}$
^6H	5	$-\frac{1}{3}\sqrt{\frac{715}{14}}$
^7F	6	$-\sqrt{5}$
^8S	7	0

Table 2

Components of the tensor $X_Q^{(K)}$ defined by equation (3.8) on taking $\boldsymbol{\varepsilon}' = \mathbf{t}$ and $\boldsymbol{\varepsilon} = \mathbf{u}$. Here, $(\mathbf{t} \cdot \mathbf{u})$ and $(\mathbf{t} \times \mathbf{u})$ denote the conventional scalar and vector products, respectively, of two vectors of rank one.

$$X_0^{(0)} = -\frac{1}{\sqrt{3}}(\mathbf{t} \cdot \mathbf{u})$$

$$X_0^{(1)} = \frac{\mathrm{i}}{\sqrt{2}}(\mathbf{t} \times \mathbf{u})_0$$

$$X_{\pm 1}^{(1)} = \mp\frac{1}{\sqrt{2}}(t_0 u_{\pm 1} - t_{\pm 1} u_0)$$

$$X_0^{(2)} = \frac{1}{\sqrt{6}}(3 t_0 u_0 - \mathbf{t} \cdot \mathbf{u})$$

$$X_{\pm 1}^{(2)} = \frac{1}{\sqrt{2}}(t_0 u_{\pm 1} + t_{\pm 1} u_0)$$

$$X_{\pm 2}^{(2)} = t_{\pm 1}\, u_{\pm 1}$$

Definitions in terms of Cartesian components labelled (a, b, c):

$$t_{+1} = -\frac{1}{\sqrt{2}}(t_a + \mathrm{i}t_b),\ t_0 = t_c,\ t_{-1} = \frac{1}{\sqrt{2}}(t_a - \mathrm{i}t_b)$$

$$X_{\pm 1}^{(1)} = \tfrac{1}{2}\{(\mathbf{t} \times \mathbf{u})_b \mp \mathrm{i}(\mathbf{t} \times \mathbf{u})_a\}$$

$$X_{+2}^{(2)} + X_{-2}^{(2)} = t_a u_a - t_b u_b \qquad X_{+1}^{(2)} + X_{-1}^{(2)} = -\mathrm{i}(t_c u_b + t_b u_c)$$

$$X_{+2}^{(2)} - X_{-2}^{(2)} = \mathrm{i}(t_a u_b + t_b u_a) \qquad X_{+1}^{(2)} - X_{-1}^{(2)} = -(t_c u_a + t_a u_c)$$

If $\mathbf{t} = \mathbf{u} = \mathbf{J}$, with $\mathrm{i}\mathbf{J} = \mathbf{J} \times \mathbf{J}$ and $\mathbf{J} \cdot \mathbf{J} = J(J+1)$, then $X_{\pm 1}^{(1)} = -\frac{1}{\sqrt{2}} J_{\pm 1}$.

Table 3

Combinations of polarization vectors in the attenuation coefficient averaged with respect to states of polarization in the primary beam described by $\mathbf{P} = (0, P_2, P_3)$; a method for performing the average over states of polarization is described in reference [1]. In the forward scattering geometry $\mathbf{q} = \mathbf{q}'$.

$$\| \varepsilon'.\varepsilon \| = 1$$

$$\| \varepsilon' \times \varepsilon \| = iP_2\hat{\mathbf{q}}$$

$$\| 3\varepsilon'_c\varepsilon_c - \varepsilon'.\varepsilon \| = \tfrac{1}{2}\left[(3\alpha_c^2 - 1)(1 + P_3) + (3\beta_c^2 - 1)(1 - P_3)\right]$$

$$\| \varepsilon'_b\varepsilon_c + \varepsilon'_c\varepsilon_b \| = \alpha_b\alpha_c(1 + P_3) + \beta_b\beta_c(1 - P_3)$$

$$\| \varepsilon'_a\varepsilon_c + \varepsilon'_c\varepsilon_a \| = \alpha_a\alpha_c(1 + P_3) + \beta_a\beta_c(1 - P_3)$$

$$\| \varepsilon'_a\varepsilon_a - \varepsilon'_b\varepsilon_b \| = \tfrac{1}{2}\left[(\alpha_a^2 - \alpha_b^2)(1 + P_3) + (\beta_a^2 - \beta_b^2)(1 - P_3)\right]$$

$$\| \varepsilon'_a\varepsilon_b + \varepsilon'_b\varepsilon_a \| = \alpha_a\alpha_b(1 + P_3) + \beta_a\beta_b(1 - P_3)$$

Here:

$$\alpha_a = -\sin\beta\cos\gamma$$

$$\alpha_b = \sin\beta\sin\gamma$$

$$\alpha_c = \cos\beta$$

$$\beta_a = (\cos\beta - 1)\cos\alpha\cos\gamma + \cos(\alpha + \gamma)$$

$$\beta_b = (1 - \cos\beta)\cos\alpha\sin\gamma - \sin(\alpha + \gamma)$$

$$\beta_c = \cos\alpha\sin\beta$$

The angles α,β and γ define the axes (a,b,c) relative to (x,y,z) using the Euler angles defined in reference [5].

Table 4

Axes (x,y,z) defined with respect to the geometry of the experiment, in which the primary beam, travelling in a direction defined by the unit vector $\hat{\mathbf{q}}$, is deflected through an angle θ to a direction defined by $\hat{\mathbf{q}}'$.

$$
\begin{aligned}
-2\sin(\theta/2)\,\hat{\mathbf{x}} &= (\hat{\mathbf{q}}-\hat{\mathbf{q}}') \\
2\cos(\theta/2)\,\hat{\mathbf{y}} &= (\hat{\mathbf{q}}+\hat{\mathbf{q}}') \\
\sin(\theta)\,\hat{\mathbf{z}} &= (\hat{\mathbf{q}}\times\hat{\mathbf{q}}')
\end{aligned}
$$

Axes (a,b,c) for an atom at a site labelled by the vector $\mathbf{R}_0$. Euler angles α,β and γ are defined following the scheme used in reference [5].

$$
\begin{aligned}
\hat{\mathbf{a}} &= \hat{\mathbf{x}}\,(\cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma)+\hat{\mathbf{y}}\,(\sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma) \\
&\quad -\hat{\mathbf{z}}\,\sin\beta\cos\gamma \\
\hat{\mathbf{b}} &= \hat{\mathbf{x}}\,(-\cos\alpha\cos\beta\sin\gamma-\sin\alpha\cos\gamma)+\hat{\mathbf{y}}\,(-\sin\alpha\cos\beta\sin\gamma+\cos\alpha\cos\gamma) \\
&\quad +\hat{\mathbf{z}}\,\sin\beta\sin\gamma \\
\hat{\mathbf{c}} &= \hat{\mathbf{x}}\,\cos\alpha\sin\beta+\hat{\mathbf{y}}\,\sin\alpha\sin\beta+\hat{\mathbf{z}}\,\cos\beta
\end{aligned}
$$

Polarization vectors, which describe pure σ and π polarizations; σ polarization is perpendicular to the plane of scattering, defined by $\mathbf{q}$ and $\mathbf{q}'$, and π polarization lies in the plane. With reference to the axes (x,y,z);

$$
\begin{aligned}
\boldsymbol{\varepsilon}_\sigma &= \boldsymbol{\varepsilon}'_\sigma = (0,0,1) \\
\boldsymbol{\varepsilon}_\pi &= \hat{\mathbf{x}}\,\cos(\theta/2)+\hat{\mathbf{y}}\,\sin(\theta/2) \\
\boldsymbol{\varepsilon}'_\pi &= \hat{\mathbf{x}}\,\cos(\theta/2)-\hat{\mathbf{y}}\,\sin(\theta/2)
\end{aligned}
$$